# PROPERTIES OF ASPHALTENES FROM VARIOUS ALBERTA CRUDE OILS

T. Ignasiak, A.V. Kemp-Jones and O.P. Strausz

Hydrocarbon Research Center
Department of Chemistry
University of Alberta
Edmonton, Alberta
Canada

## INTRODUCTION

Asphaltene is defined as the high molecular weight pentane-insoluble fraction of petroleum. In general, of all the petroleum fractions, asphaltene contains the greatest percentage of sulfur, oxygen and nitrogen. The structure and composition of asphaltene may vary considerably with the origin and mode of formation of the source reservoir.

Very few comparisons of asphaltene properties are available in the literature (1-4). Recently, a detailed investigation of the properties of Athabasca asphaltene was carried out (5). Chemical and spectroscopic evidence led to the proposal of an average structure in which relatively small hydrocarbon units are linked together by sulfur bridges. Since, in addition to the Athabasca deposit, there are other important oil sands and heavy oils in Alberta which also have high asphaltene contents, it was therefore of interest to study these asphaltenes and to compare their properties with those of Athabasca asphaltene.

The asphaltene sources investigated were the Cold Lake and Peace River oil sands, and Lloydminster crude oil. These asphaltenes have been further compared with the asphaltenes from Pembina light crude oil and a tar produced by steam cracking of gas oil.

## EXPERIMENTAL

The samples used were: (1) Cold Lake crude oil obtained by cold bailing from well Leming G-7 prior to steam stimulation; (2) a Peace River core obtained from Well OBS-5, location 4-21-85-18 W5 (Cadotte), depth 1868-1872 ft.; (3) Lloydminster base crude oil, sample 5431; (4) Pembina vacuum reduced pitch received January 9, 1976 from Imperial Oil Enterprises Ltd., Strathcona; (5) a tar produced by steam cracking gas oil, sample PS-76-020.

The asphaltenes were prepared as described previously (5) for Athabasca asphaltene. When the sample was found to contain large amounts of clay, a 5% solution of the asphaltene in benzene was centrifuged at 4000 rpm for several hours, and decanted, and the asphaltene was then reprecipitated with pentane.

The experimental conditions for the reductive octylation and silylation are given in detail in a previous paper (5).

The molecular weights were determined by vapor pressure osmometric method at a nominal asphaltene concentration of 20 mg/ml in benzene. Infrared spectra were determined at 0.004 M concentration in carbon tetrachloride solution in a 5 mm cell.

The $^{13}C$ NMR spectra, recorded as described previously (5), can be integrated numerically using a subroutine provided by Bruker Scientific.

## RESULTS AND DISCUSSION

Elemental analyses and average molecular weights for the asphaltene samples used in this study are shown in Table I. The analyses of the Cold Lake, Peace River and Lloydminster asphaltenes show little to distinguish them from Athabasca asphaltene, the main difference being a trend toward higher molecular weights and a higher sulfur content in the Peace River sample. The asphaltene from the light Pembina oil is different however. It represents only a minute percentage of the oil, as expected from

the viscosity, and is very low in sulfur content. The average molecular weight is lower than that of Athabasca asphaltene, and definitely lower than the average molecular weight of the high sulfur asphaltenes. It is clear that any conclusion about the structure of Athabasca asphaltene should not be extended to the trace amount of asphaltene in light oils.

The Pembina asphaltene has properties, e.g. m.w. and heteroatom content, intermediate between those of the heavy oil asphaltenes and steam cracking tar asphaltene. This very viscous refinery tar contains a large amount of asphaltene, which is even lower in heteroatoms than the asphaltenes from the light oils, and has a low molecular weight and low H/C ratio.

The routine (2% solution in a 0.5 mm cell) IR spectra of the asphaltenes studied appeared to be quite similar. Some differences, however, in the hydrogen stretching region at 3600-3000 $cm^{-1}$ become apparent from 0.004 M solutions of asphaltenes measured in a 5 mm cell (Figure 1). The IR spectrum of Cold Lake asphaltene was not suitable for interpretation because of extremely high background interference. Asphaltene precipitated from Peace River bitumen shows a broad hydrogen bonding absorption with a maximum centered about 3250 $cm^{-1}$; its shape and intensity approximates that of Athabasca asphaltene (6). The free phenolic and/or alcoholic absorptions at 3600 $cm^{-1}$ and the free NH absorption at 3480 $cm^{-1}$ are observable in the spectrum of Lloydminster asphaltene, and the hydrogen bonded absorption is clearly reduced as compared to Athabasca and Peace River asphaltenes. In Pembina asphaltene the relative intensity of the free OH absorption is very weak and no hydrogen bonding is visible.

Thus, the almost complete association of the OH and likely NH functional groups seems to be a characteristic feature of asphaltene originating from Alberta oil sands. The difference in the role which hydrogen bonding plays in the molecular aggregation of Athabasca, Cold Lake, Peace River asphaltenes and those from Lloydminster and Pembina crudes is clearly demonstrated by the silylation reaction. On silylation, hydroxyl groups are generally easily converted to trimethylsilyl derivatives. This is accompanied by the disappearance of IR absorption in the hydrogen stretching region and the appearance of the absorption of trimethylsilyl ethers. The IR spectra of silylated Athabasca, Peace River and Lloydminster asphaltenes all show a remarkable reduction in the hydrogen bonding absorption and the free OH absorption disappears in the latter. As seen from data given in Table II, the molecular weights of silylated Athabasca, Cold Lake and Peace River asphaltenes have been drastically reduced, roughly by half, pointing to the intermolecular character of the hydrogen bonding. The decrease in the molecular weight of Lloydminster asphaltene is less significant and none occurs for Pembina asphaltene, as expected from their IR spectra.

There is not much variation in the oxygen contents (average of 2%) of the asphaltenes studied (Tables I and II), and the number of silyl groups attached to asphaltenes, calculated from either integration of the PMR spectrum or changes in the H/C ratios and ash contents, indicates that from 60 to 64% of the oxygen in Athabasca, Cold Lake and Peace River asphaltenes, 71% in Lloydminster and 23% in Pembina asphaltenes is accessible for silylation. Some of this "silylated" oxygen may originate from oxygen functional groups other than hydroxyl (7). The disappearance on silylation of the small but distinct carbonyl absorption at 1725 $cm^{-1}$, which is present in all except Athabasca asphaltenes may suggest the existence of readily enolized ketones, for example.

That most of the nitrogen in asphaltenes is present in the form of NH groups is concluded from the IR absorption at 3480 $cm^{-1}$ previously (8) assigned to free NH groups. The changes in this region before and after silylation indicate that the NH groups play an important role in hydrogen bonding in Athabasca, Cold Lake and Peace River asphaltenes, and almost none in Lloydminster and Pembina asphaltene; in general they are not easily silylated.

The $^{1}H$ and $^{13}C$ NMR spectra of the heavy oil asphaltenes are qualitatively similar to those of the Athabasca asphaltene (5). The quantitative proportions of aromatic hydrogen and carbon are shown in Table III. The NMR spectra of the refinery tar show that it contains 47% aromatic hydrogen and 87% aromatic carbon which emphasizes its difference from Athabasca asphaltene. These values make it of interest for the application of the structural analysis method we reported previously (5). The H/C ratio of 0.71 means that there are 65 double bond equivalents (DBE)/100 C. Using the value of 0.72 for DBE/aromatic carbon which was assumed for Athabasca asphaltene (5),

and the 87% aromatic carbon from $^{13}C$ NMR, gives 87 x 0.72 = 62.6 DBE/100 C due to aromatic carbon atoms. This is sufficiently close to the 65 total DBE/100 C that the DBE due to alicyclic carbon atoms can be assumed to be zero. To some extent this is expected from the method of preparation of the steam cracking asphaltene, and lends support to the value of 0.72 for DBE/aromatic carbon which we assumed for Athabasca asphaltene. A structure consistent with the H/C ratio and the $^{1}H$ and $^{13}C$ NMR spectra is as shown in Figure 2. It has H/C ratio 0.72 (0.71 observed), 88% aromatic carbon (87% observed) and 50% aromatic hydrogen (47% observed). To obtain a proportion of aromatic hydrogen as low as 47% with 87% aromatic carbon requires that virtually all the aliphatic groups are methyl groups, to maximize the substitution on the aromatic rings.

To further compare the various heavy oil asphaltenes, they were reduced and octylated following the procedure (5) used for Athabasca asphaltene. Reaction of the Athabasca asphaltene with potassium in tetrahydrofuran in the presence of naphthalene gave an impressive decrease in the m.w. of the asphaltene which, on the basis of some other auxiliary studies involving determination of oxygen distribution and model reduction of sulfur compounds, could be attributed to the cleavage of non-ring sulfur. From the results shown in Table IV some differences become apparent. In all cases the m.w. of the product, corrected for octyl groups added and by-products, is higher than that found for Athabasca asphaltene, although there is still a substantial decrease in m.w. on reduction. The m.w., number of octyl groups added, desulfurization, and weight increase all follow the same pattern, with the order of reactivity being Cold Lake > Peace River > Lloydminster. Since the sulfur content of these asphaltenes is similar to that of Athabasca asphaltene (Table I), it follows that a greater proportion of the sulfur atoms are in rings. The percentage of sulfur in bridges was estimated from the ratio of the number of bonds cleaved on reduction to the number of sulfur atoms present in a molecule.

The number of bonds cleaved (N) was derived from the experimental molecular weights using an equation: N = MW starting/MW reduced - 1, in which the molecular weight of the silylated asphaltenes was taken as MW starting.

## CONCLUSIONS

In the present study it has become clearly established that asphaltenes from Alberta heavy oil deposits have much in common, including concentration in the bitumen, elemental composition, high molecular weight, high sulfur content and an oxygen distribution such that most of the oxygen is in hydroxyl groups. Asphaltenes from the typical oil sands exhibit very strong hydrogen bonding properties, partly intermolecular in character, whereas in the Lloydminster asphaltene, the hydroxyl association is much less pronounced.

The results from reductive octylation indicate that all these sulfur-rich asphaltenes possess a sulfur-polymer framework. The amount of sulfur in bridges, however, varies, decreasing in the order Athabasca > Cold Lake > Peace River > Lloydminster, which may reflect some diagenic differences among the asphaltene sources.

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TABLE 1

Elemental Analyses and Molecular Weights of Various Asphaltenes

| Asphaltene Source | % of Source | %, Wt., d.a.f. C | H | N | S | O | Ash | H/C | MW |
|---|---|---|---|---|---|---|---|---|---|
| Athabasca | 16 | 80.3 | 8.0 | 1.2 | 8.2 | 2.5 | 1.5 | 1.20 | 5920 |
| Cold Lake | 15 | 80.2 | 7.8 | 1.1 | 8.3 | 2.5 | 4.2 | 1.17 | 8140 |
| Peace River | 17 | 79.4 | 8.0 | 0.8 | 9.1 | 2.6 | 4.0 | 1.22 | 9510 |
| Lloydminster | 9 | 81.2 | 8.0 | 1.0 | 8.4 | 1.5 | 1.2 | 1.18 | 9300 |
| Pembina Pitch | 3 | 86.8 | 9.2 | 0.9 | 1.0 | 2.0 | 0.1 | 1.27 | 3100 |
| Steam Cracking Tar | 20 | 91.8 | 5.4 | 0.0 | 0.6 | 0.4 | 1.2 | 0.71 | 1380 |

TABLE 2

The Effect of Silylation on Various Asphaltenes

| Asphaltene Source | MW After Silylation | Number of atoms or groups/100 C atoms Oxygen | Trimethyl-silyl | % of Oxygen Silylated |
|---|---|---|---|---|
| Athabasca | 3680 | 2.3 | 1.5 | 64 |
| Cold Lake | 4600 | 2.4 | 1.5[1] | 63 |
| Peace River | 4430 | 2.5 | 1.6 | 64 |
| Lloydminster | 7150 | 1.4 | 1.0 | 71 |
| Pembina | 3070 | 1.7 | 0.4[2] | 23 |

[1] NMR spectrum is broadened and unresolved, the number of silyl groups was determined from changes in the H/C ratio and ash content.
[2] The NMR of silylated Pembina asphaltene does not show any absorption near δO., though there was some change in H/C ratio and ash content.

TABLE III

Content of Aromatic Hydrogen and Aromatic Carbon in Various Asphaltenes

| Asphaltene | % ArH | % ArC |
|---|---|---|
| Athabasca | 8 | 42 |
| Cold Lake | -[a] | 30 |
| Peace River | 9 | 35 |
| Lloydminster Crude | 5 | 42 |
| Steam Cracking Tar | 47 | 87 |

[a] Spectrum broadened and unresolved, probably due to an unusually high content of paramagnetic molecules. This effect was also visible in the $^{13}C$ spectrum.

TABLE IV

Reductive Octylation of Alberta Asphaltenes[1]

| Asphaltene | MW Octyl Free | No. of Octyl Groups Added/100C | Weight Increase % | % of Sulfur Removed | No. of Bonds Cleaved | % of Sulfur in Bridges |
|---|---|---|---|---|---|---|
| Athabasca | 580 | 9.4 | 120 | 37 | 5.3 | 65 |
| Cold Lake | 1280 | 7.9 | 65 | 52 | 2.6 | 22 |
| Peace River | 1590 | 7.1 | 53 | 45 | 1.8 | 14 |
| Lloydminster | 2010 | 6.3 | 48 | 32 | 2.6 | 13 |

[1] Data are the means of two experiments.

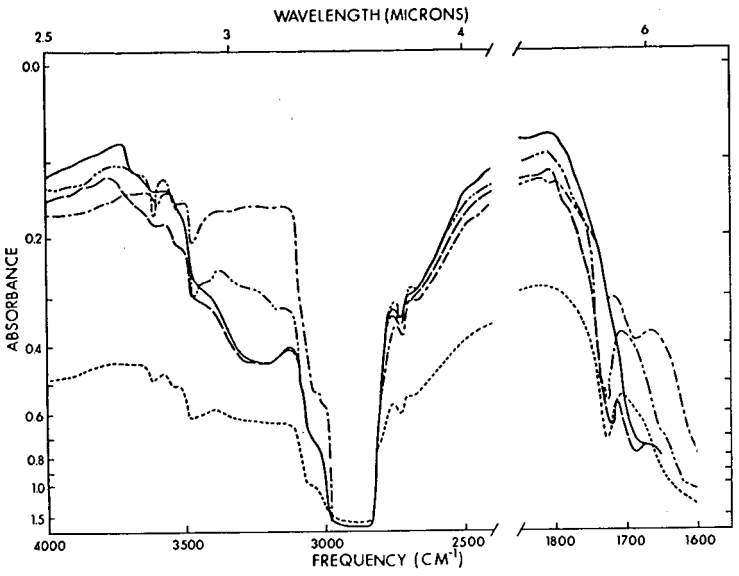


FIGURE 1

Infrared spectra of some Alberta asphaltenes - the hydrogen and carbonyl streching regions.

| | |
|---|---|
| Athabasca | ——— |
| Cold Lake | - - - - - - - - |
| Peace River | — — — — — |
| Lloydminster | — · — · — · — |
| Pembina | — · · — · · — · · |

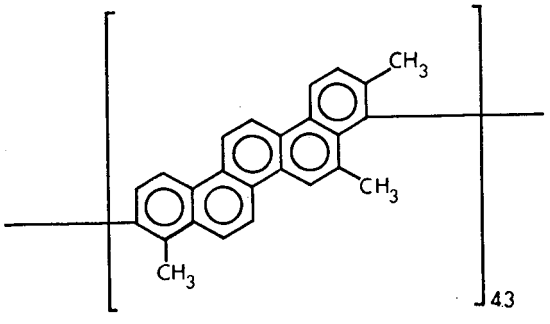


FIGURE 2